

# **Photochemistry and dilution of Asian air pollution episodes transported to the Northwest U.S.**

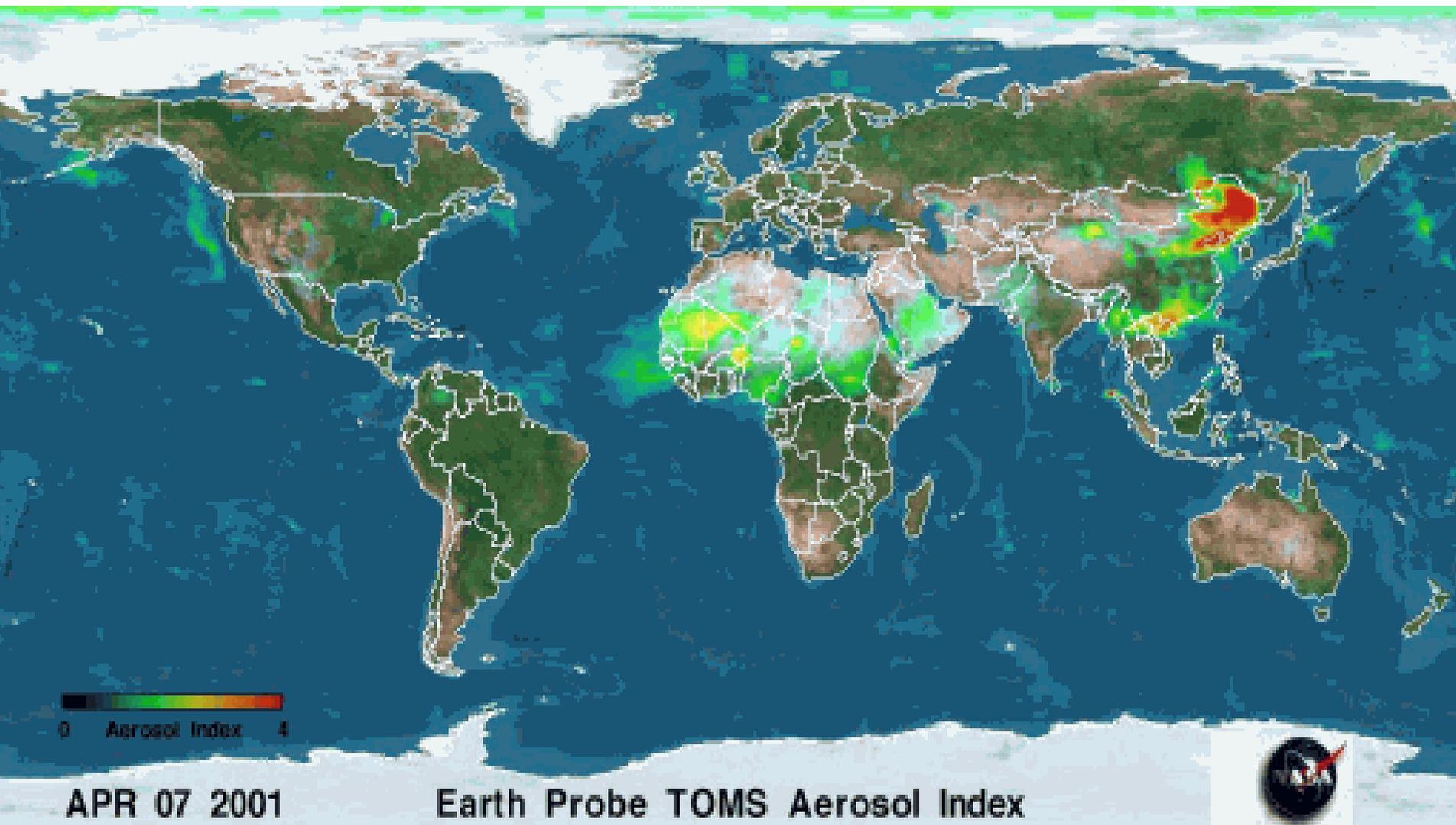


**17 August 2004 GCEP Workshop**

**Heather Price**

**Chemistry • University of Washington**

# Asia is a significant source of natural and anthropogenic air pollutants



# Cheeka Peak



# PHOBEA Experiments 1997-2003

Aircraft  
Vertical  
Profiles

Cheeka  
Peak

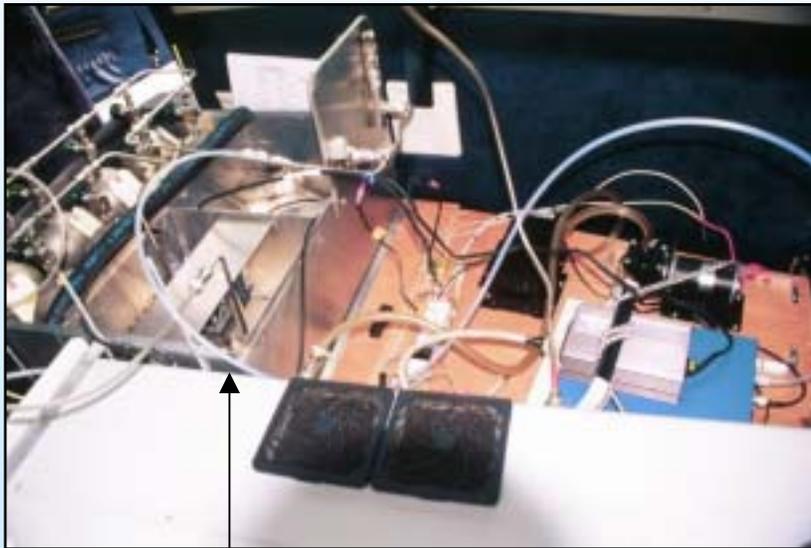


Beechcraft Duchess



# PHOBEA Research Aircraft

Beechcraft Duchess



Canister Sampler  
CO and NMHCs

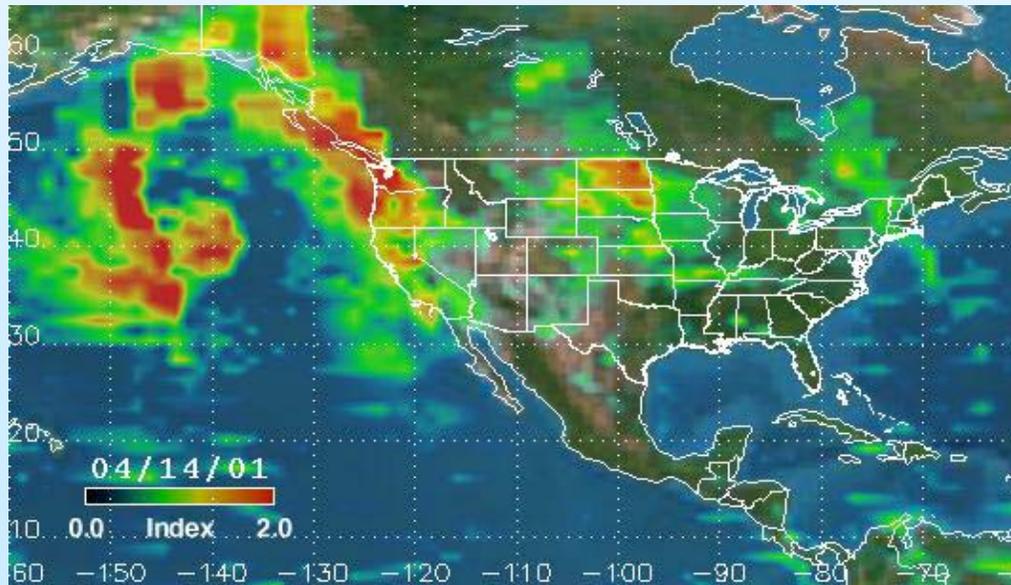
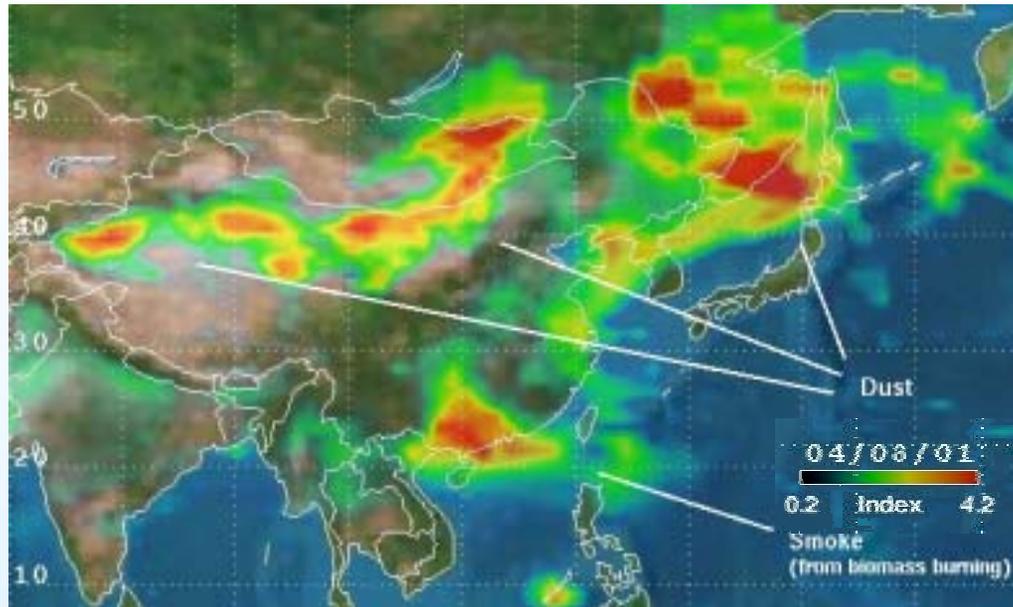
2B Ozone Analyzer

TSI Nephelometer





# Earth Probe Satellite TOMS Aerosol Index



# Eleven PHOBEA Long Range Transport (LRT)

Episodes observed at CPO and from Aircraft

1997, 1999, 2001, 2002



# Springtime PHOBEA LRT Episodes 1997-2002

Date	PHOBEA	Transit	$\sigma_{sg} \text{ M m}^{-1}$		Ozone ppbv		CO ppbv	
	Altitude	Time	Actual	$\Delta$	Actual	$\Delta$	Actual	$\Delta$
29-Mar-97	0.5	6.0	19	10	45	1	173	22
9-Apr-99	2.9	7.5	21	19	67	9	171	39
29-Mar-01	2.2	6.5	20	17	72	27	167	18
14-Apr-01	4.9	5.8	25	22	44	-2	184	56
6-May-01	2.9	8.0	12	11	58	11	153	15
27-Mar-02	0.5	5.0	4	8	47	2	187	36
15-Apr-02	4.9	5.5	18	17	75	14	233	97
20-Apr-02	0.5	8.0	10	2	43	-2	183	32
14-May-02	4.4	9.5	21	19	75	17	180	29
17-May-02	4.0	10.0	31	29	77	19	194	43
23-May-02	4.2	8.0	29	27	79	21	188	37
Median	2.9	7.5	20	17	67	11	183	36

# **Case Study**

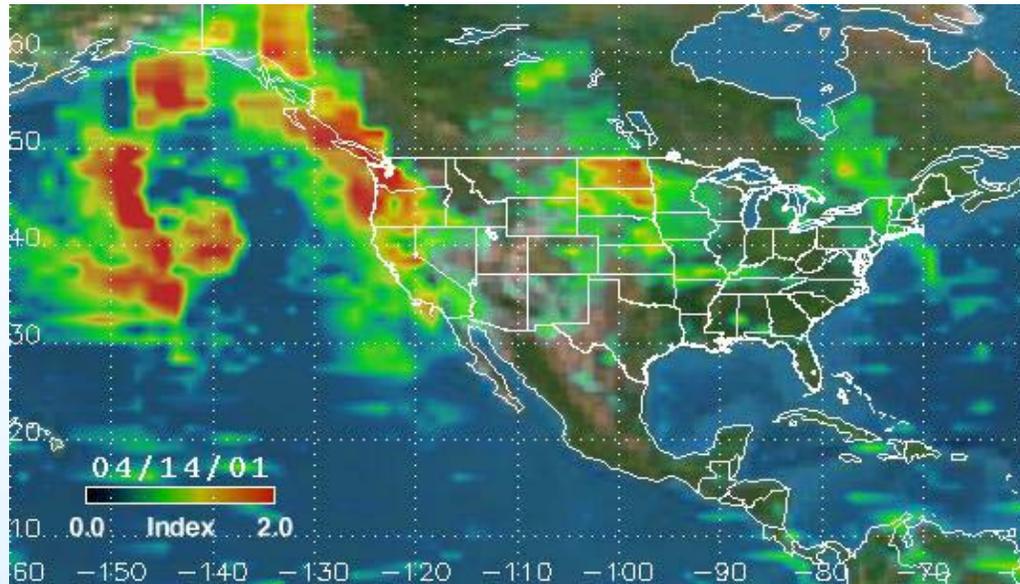
## **2001 PHOBEA Aircraft Data**



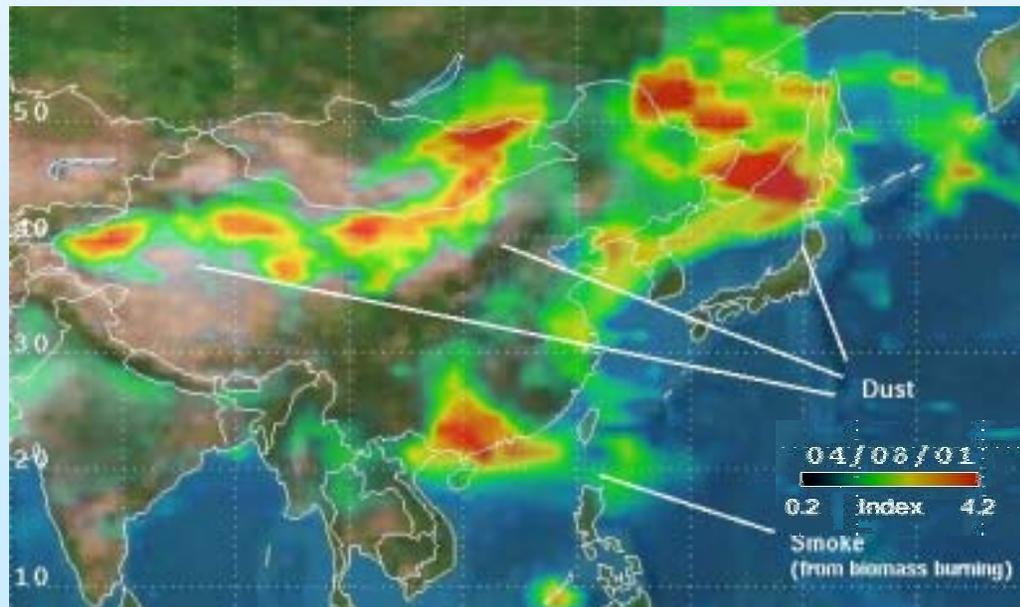
**April 14, 2001**

# TOMS Aerosol Index

14 April 2001



8 April 2001



# Dust Storm darkens NE China 7 April 2001

Jilin Province, China  
April 7 and 8, 2001

(NE of Beijing appx. 45.5N, 122.5E).



Daytime photos from the  
same location one day apart.

# Dust Storm reaches the Grand Canyon

## 15 April 2001



A normal relatively clear day



Hazy from Asian Dust on April 15

Photos by Alan Piper

# Dust Storm reaches Navajo Mountain

## 16 April 2001

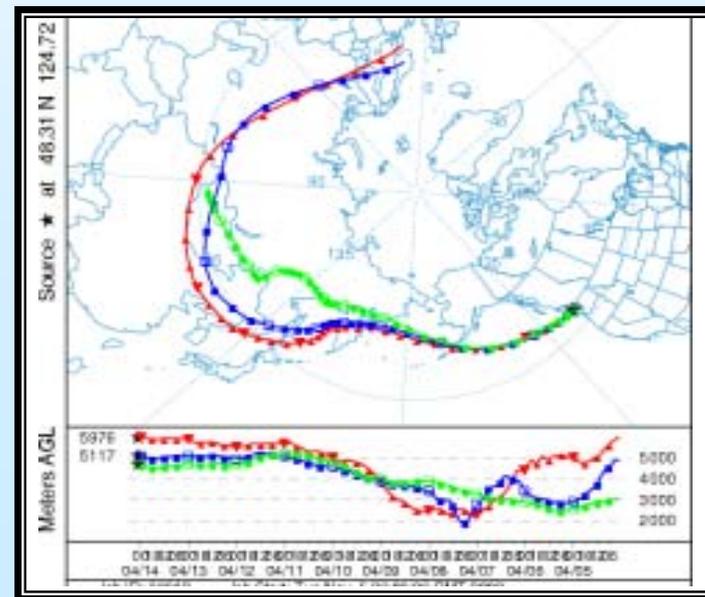
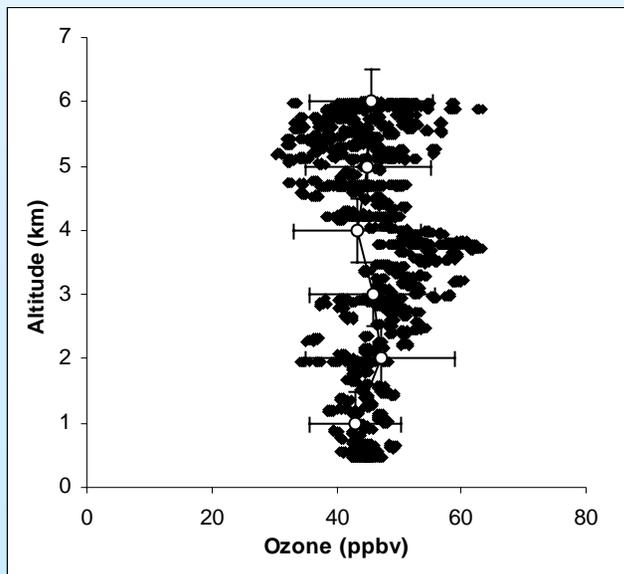
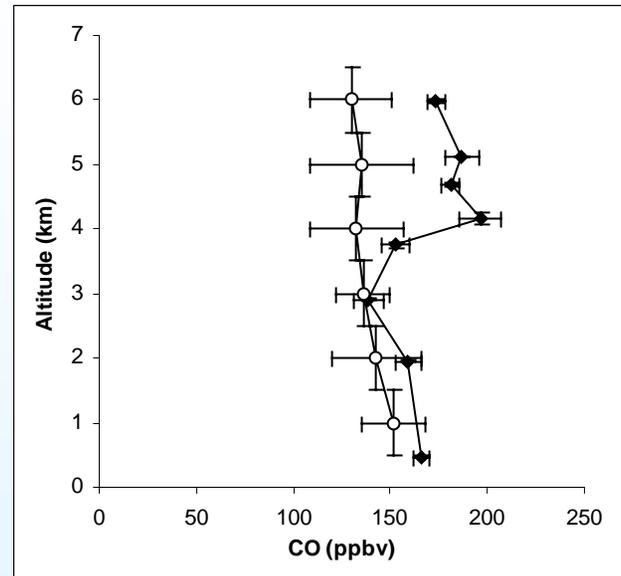
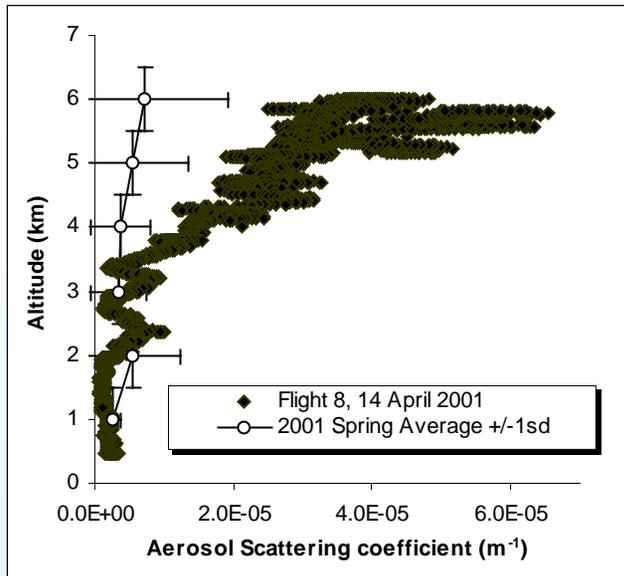


Page, Arizona looking East toward Navajo Mountain on a relatively clear day



Same place, hazy from Asian Dust on April 16

# Aircraft observations on 14 April 2001



<sup>a</sup>Spring 2001 means at 3.5-6km [Price et al., 2003]

## CO

### Sources:

Combustion



biomass burning

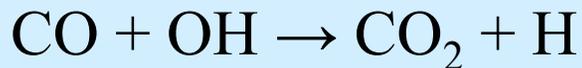
fossil fuels

CH<sub>4</sub> oxidation

Natural emissions

### Sinks:

Reaction with hydroxyl:

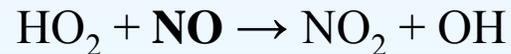
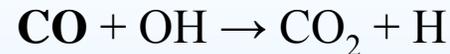


## Tropospheric O<sub>3</sub>

### Sources:

Photochemical 

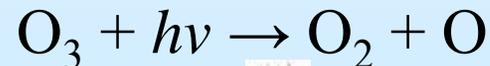
(CO, NMHCs + NO<sub>x</sub> +  $h\nu$ )



Stratospheric

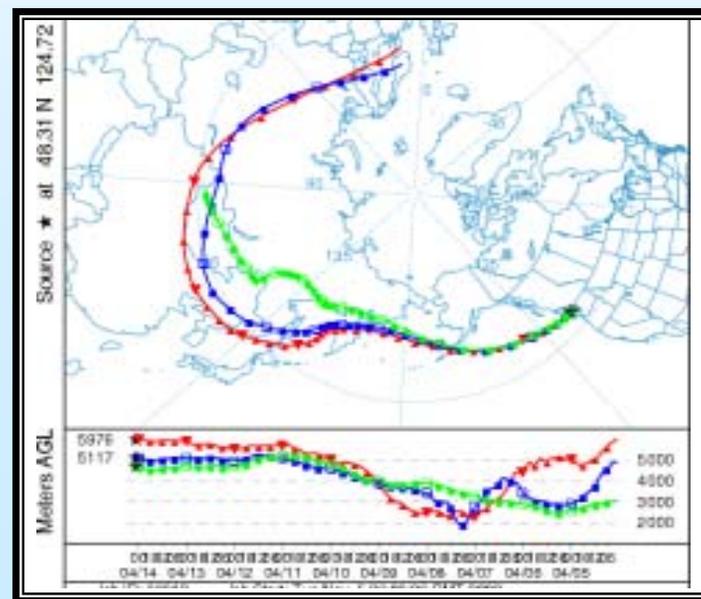
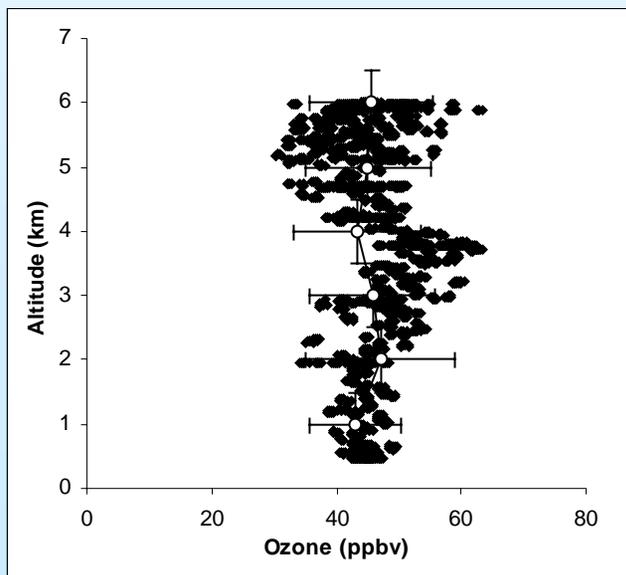
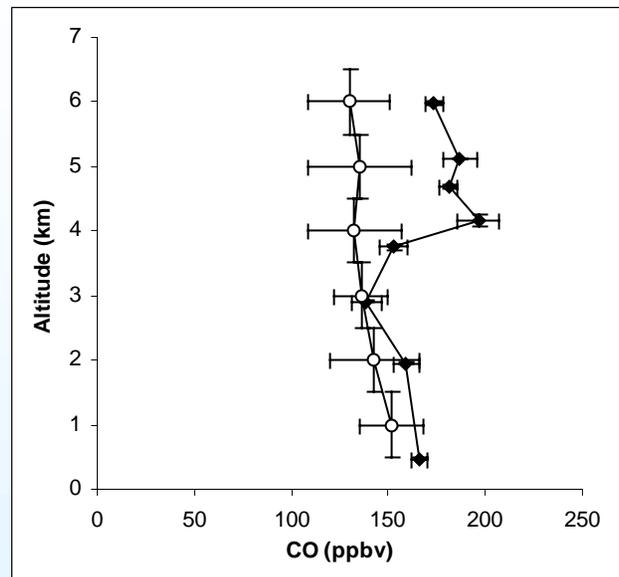
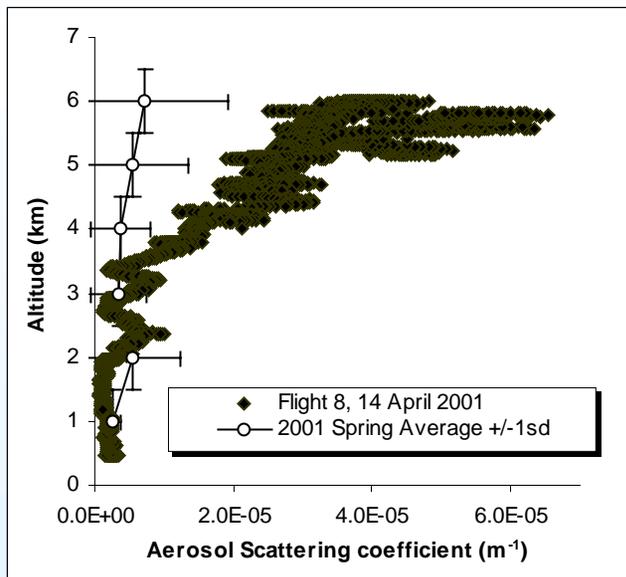
### Sinks:

Photolysis 



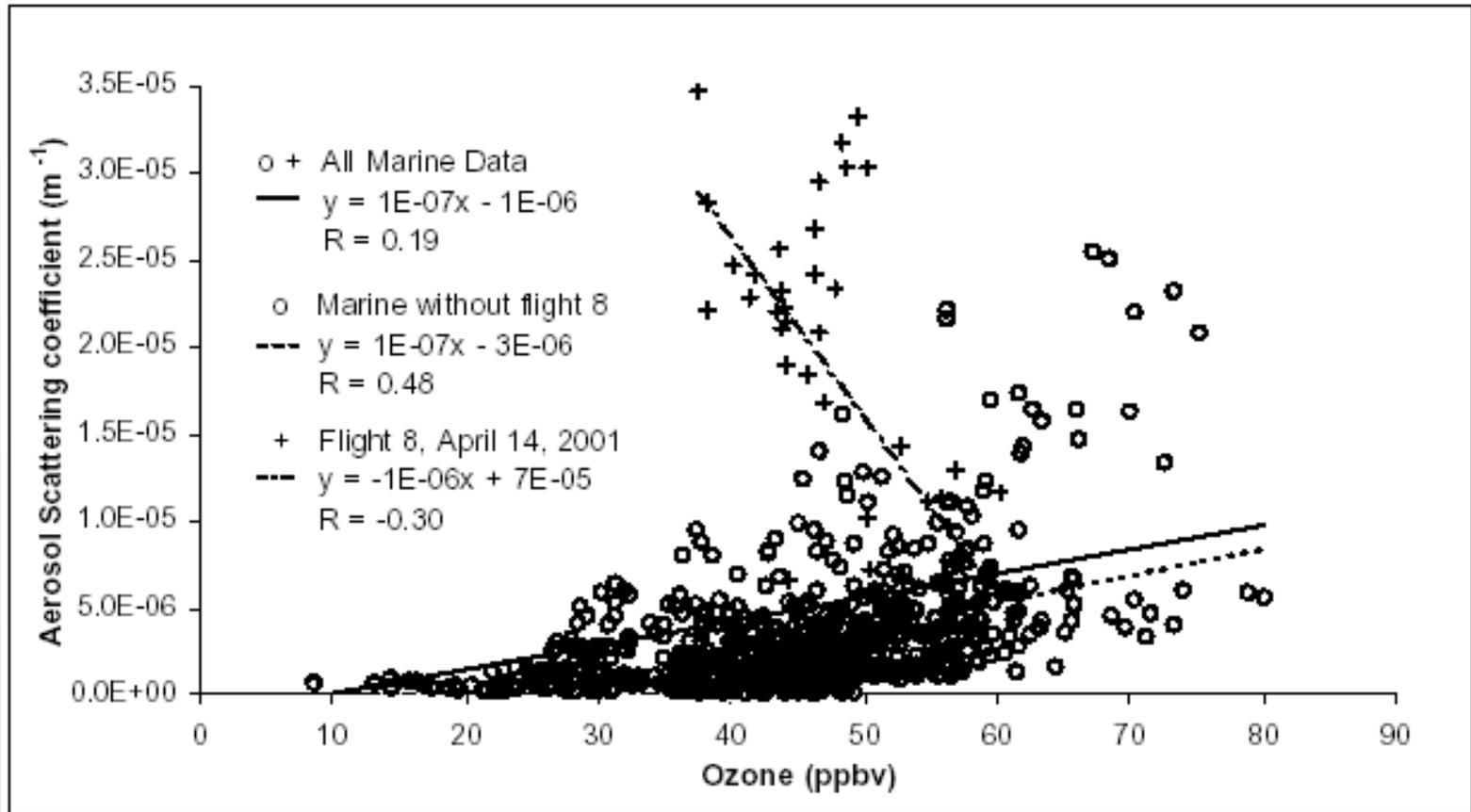
Deposition 

# Aircraft observations on 14 April 2001



<sup>a</sup>Spring 2001 means at 3.5-6km [Price et al., 2003]

# PHOBEA 2001 Relationship between Aerosols & Ozone



# Dust Storm darkens NE China 7 April 2001

Jilin Province, China  
April 7 and 8, 2001

(NE of Beijing appx. 45.5N, 122.5E).

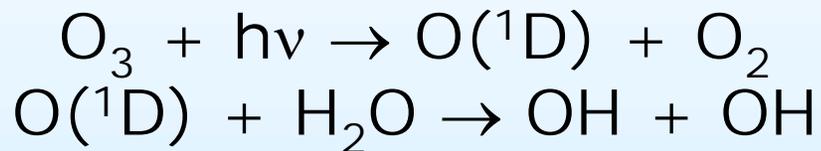


Daytime photos from the  
same location one day apart.

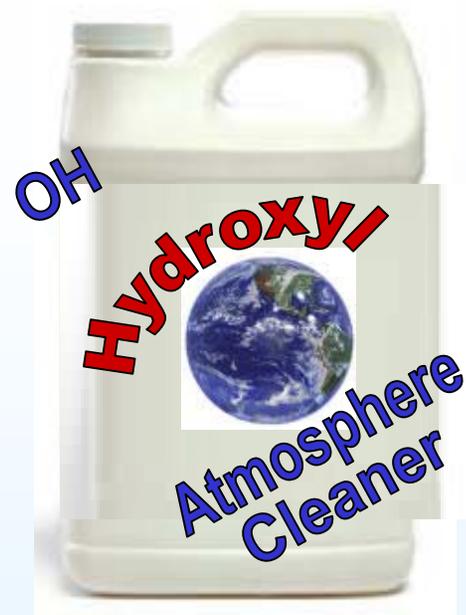
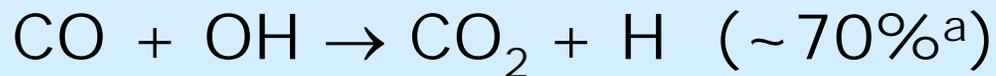
# The Hydroxyl Radical (OH)

The most important oxidant in the atmosphere

- Major source:

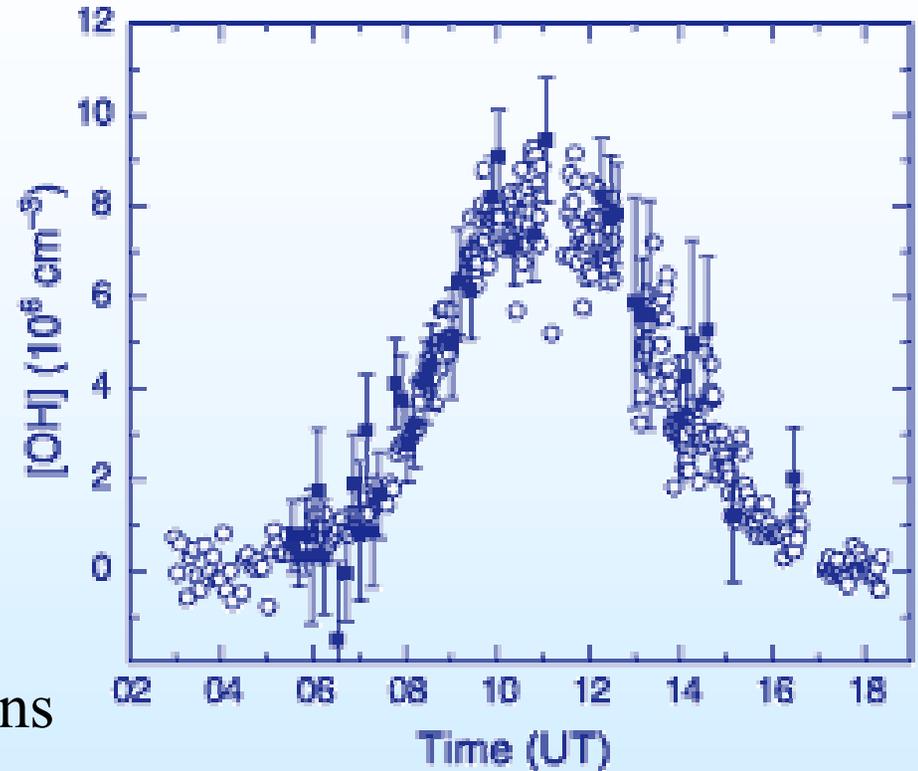


- Major sink:



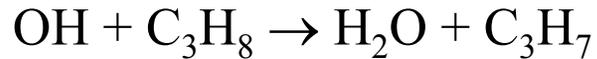
# The Hydroxyl Radical

- Typical background levels are very low  $\sim 10^6$  molecules  $\text{cm}^{-3}$
- Methods for measuring directly are limited:
  - optical spectroscopy (DOAS, LIF), chemical conversion of OH, radiocarbon
- Calculating OH from observations of other species – proxy methods (methylchloroform, NMHCs)



Diurnal variation of OH measured using LIF (o) and DOAS ( $\square$ ) during POPCORN (Adapted from Hofzumahaus *et al.*, 1998).

# Using NMHCs To Determine [OH]



$$[\text{C}_3\text{H}_8]_t = [\text{C}_3\text{H}_8]_0 e^{-k[\text{OH}]t}$$

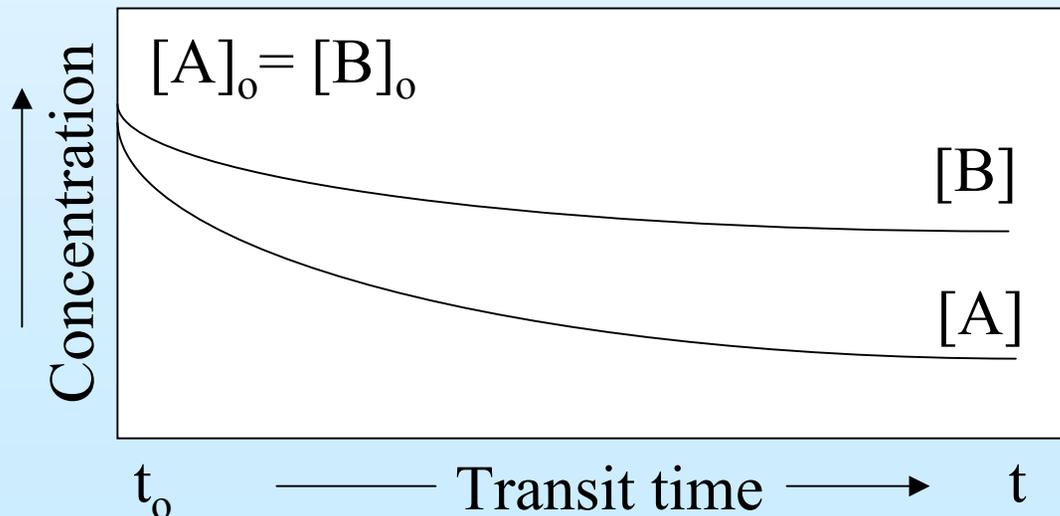
Light alkanes, NMHCs,  
main sink is bimolecular  
reaction with hydroxyl (OH)

NMHC lifetimes vary  
allowing for [OH] or transit  
determination:

Butane ~ 5 days

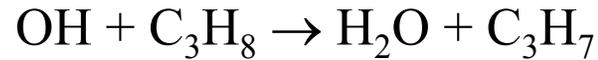
Propane ~ 10 days

Ethane ~ 50 days



B (propane) = longer  $\tau$   
A (n-butane) = shorter  $\tau$

## Using NMHCs To Determine [OH]



$$[\text{C}_3\text{H}_8]_t = [\text{C}_3\text{H}_8]_0 e^{-k[\text{OH}]t}$$

By using two NMHCs with different lifetimes with respect to OH and an estimate of transit time from backward trajectories, can estimate OH using the following equation<sup>a</sup>:

$$[\text{OH}]_{\text{average}} = \frac{\ln \frac{[A]}{[B]} - \ln \frac{[A]_0}{[B]_0}}{(k_b - k_a)t_r}$$

$t_r$  = transit time

$k$  = rate constants wrt OH

[OH] in mlcl/cm<sup>3</sup>

$A$  &  $B$  = alkane mixing ratios

## Assumptions for calculating [OH]

- Advective transport dominates over turbulent mixing
- Trajectories represent accurate transit time
- Negligible mixing with aged/diluted airmasses
- Negligible injection of fresh emissions en route
- The observations and emissions of hydrocarbon ratios represent the source/ upwind airmass

Source Data in [OH] calculations	$C_4H_{10}/C_3H_8$ Ratios
PEM-West B 1994	0.37
ACE-Asia <sup>a</sup> 8-April-2001	0.34
ACE-Asia <sup>a</sup> 11-April-2001	0.35
2001 Trace-P Jilin Province <sup>b</sup>	0.37

<sup>a</sup> Tai Chen's GC-FID aircraft measurements.

<sup>b</sup> David Streets 2000 emission Inventories (Streets et al., 2003).

## Limitations in Determining [OH]

- More reactive hydrocarbon [A] approaching detection limit will cause underestimate of [OH]
- Injection of Fresh hydrocarbons (increased [A]) will also cause an underestimate of [OH].
- Injection of Aged hydrocarbons (increased [B]) or dilution will cause an overestimate of [OH].

$$[\text{OH}]_{\text{average}} = \frac{\ln \frac{[A]}{[B]} - \ln \frac{[A]_o}{[B]_o}}{(k_b - k_a)t_r}$$

## [OH] Results (molecules cm<sup>-3</sup>)

$$[\text{OH}]_{\text{average}} = \frac{\ln \frac{[A]}{[B]} - \ln \frac{[A]_o}{[B]_o}}{(k_b - k_a)t_r}$$

Mean	7.1x10 <sup>5</sup>
Median	6.3x10 <sup>5</sup>
σ	2.9x10 <sup>5</sup>

Date	PHOBEA Altitude	Transit Altitude	OH <sub>24 hr</sub>
29-Mar-97	0.5	0.7	5.5E+05
9-Apr-99	2.9	3.0	5.7E+05
29-Mar-01	2.2	3.5	5.6E+05
14-Apr-01	4.9	4.2	1.9E+05
6-May-01	2.9	3.3	8.8E+05
27-Mar-02	0.5	0.4	5.0E+05
15-Apr-02	4.9	5.0	1.0E+06
20-Apr-02	0.5	2.3	8.1E+05
14-May-02	4.4	2.3	8.7E+05
17-May-02	4.0	2.1	6.3E+05
23-May-02	4.2	6.8	1.3E+06
Median	2.9	3.0	6.3E+05

# Calculating [OH] for April 14, 2001 ~ including dilution ( $K_{dil}$ )

$dX/dt$  = - photochemical loss – entrainment of background air

$$dX/dt = - k_x X [OH] - K_{dil} (X - X_b)$$

Solution to the 1<sup>st</sup> order differential eqn:

$$X = \frac{K_{dil} X_b}{K_{dil} + [OH] k_x} + \left( X_o - \frac{K_{dil} X_b}{K_{dil} + [OH] k_x} \right) e^{-t(K_{dil} + [OH] k_x)}$$

# Calculating Dilution

**The two methods for determining dilution:**

- **Chemical Method**
- **Meteorological Method**

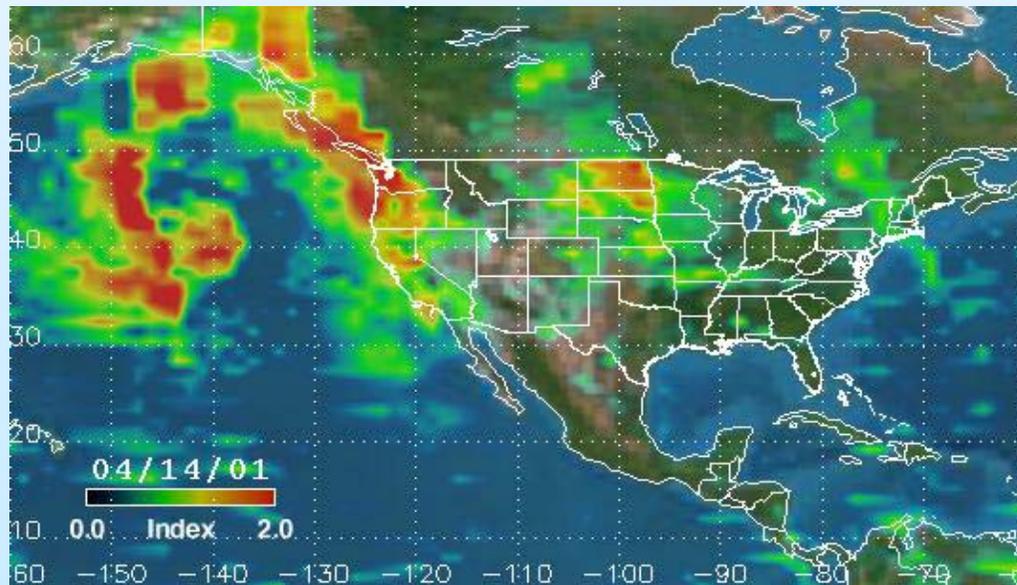
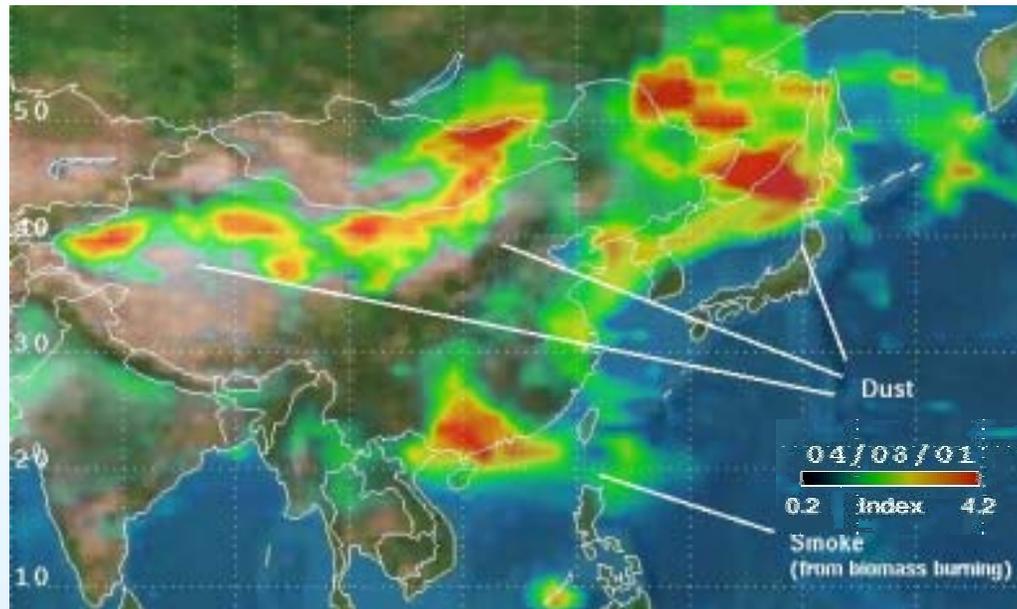
# Calculating Dilution Using Chemical Method

$$dX/dt = - \cancel{\text{photochemical loss}}^0 - \text{entrainment of background air}$$

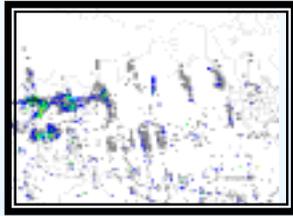
$$dX/dt = - \cancel{[\text{OH}]r_x X}^0 - K (X - X_b) = - K (X - X_b)$$

$$K_{dil} = \frac{1}{t} \ln\left(\frac{X_i - X_b}{X - X_b}\right)$$

# Pseudo-chemical: TOMS Aerosol Index

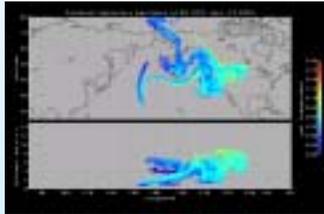


# Calculating Dilution Using Meteorological Method



HYSPLIT

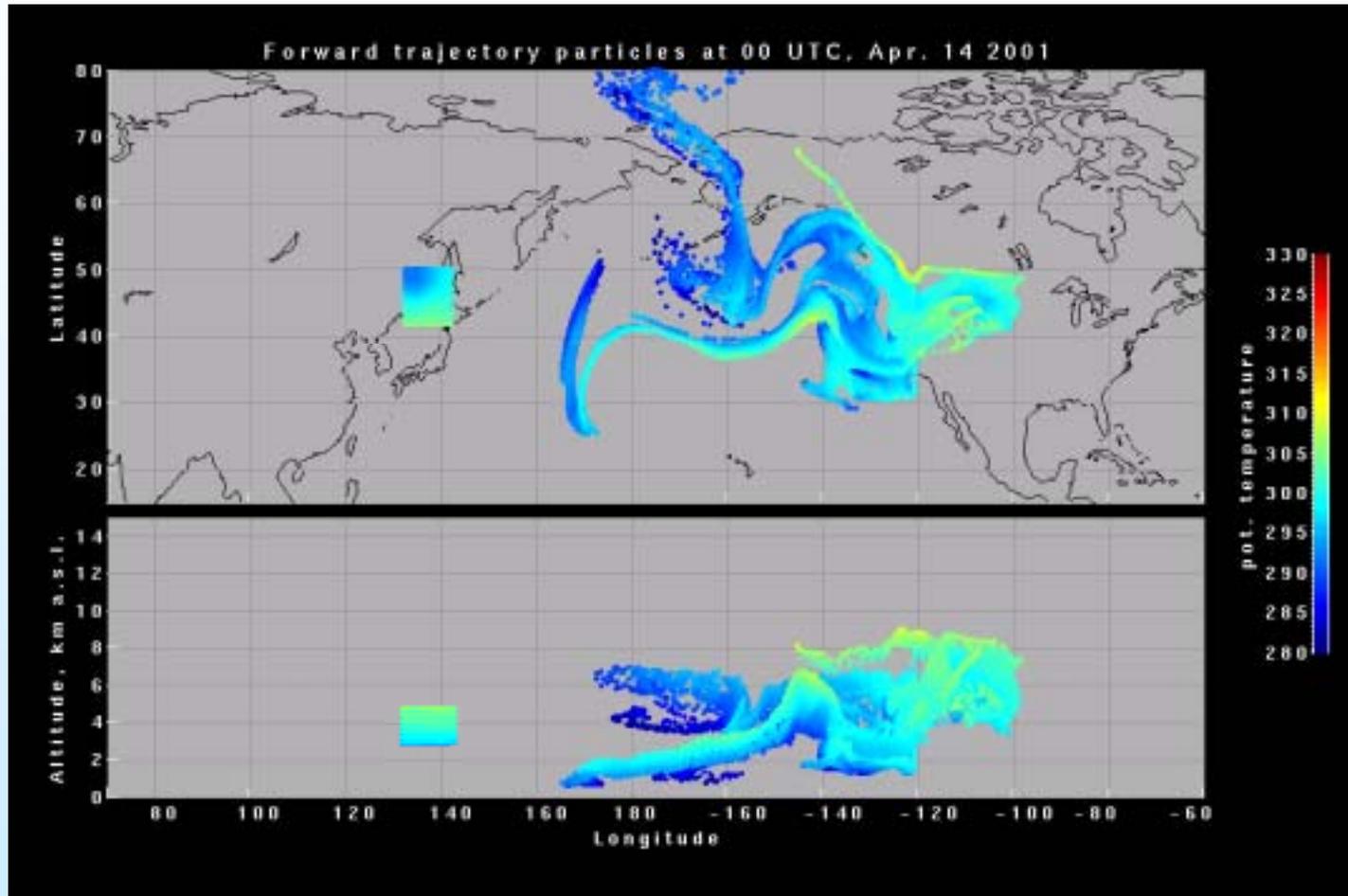
– Dr. Rowland Draxler



NOAA Aeronomy Lab

– Dr. Owen Cooper

# NOAA Aeronomy Lab Model



# Calculating Dilution for 14 April 2001

$$K_{dil} = \frac{1}{t} \ln\left(\frac{X_i - X_b}{X - X_b}\right)$$

## Chemical and Meteorological Methods

Results ( $k_{dil}=0.010\pm0.004$ )

Species	$X_i$	$X$	$X_b$	Dilution factor ( $k_{dil}$ ) $\text{hr}^{-1}$
Ethane <sup>a</sup>	2801	1613	1220	0.0097
Ethane <sup>b</sup>	3771	1613	1220	0.0130
CO <sup>b</sup>	300	177	131	0.0090
TOMS-AI	4.2	2.0	0.0	0.0052*
HYSPLIT	9.6e-10	4.84e-10	0.0	0.0048
FABtraj <sup>c</sup>	1000	20.0	0.0	0.0112
FABtraj <sup>d</sup>	1000	12.5	0.0	0.0144
Mean				0.010 ± 0.004

\* Considerable uncertainty.

## The final step: Calculating OH

$dX/dt = -$  photochemical loss – entrainment of background air

$$dX/dt = - K_{dil} (X - X_b) - k_x X [OH]$$

$$X = \frac{K_{dil} X_b}{K_{dil} + [OH] k_x} + \left( X_o - \frac{K_{dil} X_b}{K_{dil} + [OH] k_x} \right) e^{-t(K_{dil} + [OH] k_x)}$$

## Preliminary [OH] result for 14 April 2001

$$X = \frac{K_{dil} X_b}{K_{dil} + [\text{OH}] k_x} + \left( X_o - \frac{K_{dil} X_b}{K_{dil} + [\text{OH}] k_x} \right) e^{-t(K_{dil} + [\text{OH}] k_x)}$$

Species	$X$	$X_i$	$X_b$	[OH]
Propane	462	1190	270	$3 \times 10^5$
Ethyne	427	1048	232	$1 \times 10^5$

Using  $K_{dil} = 0.010 \text{ hr}^{-1}$

Previous OH calc method:  $2 \times 10^5 \text{ molecules cm}^{-3}$

# Conclusions

- OH calculation results:
  - Method 1:  $7.1 \times 10^5 \pm 2.9 \times 10^5$  molecules  $\text{cm}^{-3}$   
 $1.9 \times 10^5$  molecules  $\text{cm}^{-3}$
  - Method 2 (incl  $K_{dil}$ ):  $3 \times 10^5$  &  $1 \times 10^5$  molecules  $\text{cm}^{-3}$
- Dust and BL episodes have lowest  $\text{O}_3$  and  $[\text{OH}]$  levels attributed to heterogeneous chemistry, MBL loss processes
- Dilution from chemical and meteorological methods:
  - using CO, Ethane, AI<sup>TOMS</sup>, NOAA-AL, HYSPLIT:  
 $0.010 \pm 0.004$   $\text{hr}^{-1}$

# Thanks!

- Dan Jaffe
- Paul Doskey
- Owen Cooper
- Lyatt Jaeglé
- Isaac Bertschi
- Peter Weiss
- J.B. Dennison
- Julie Snow
- Anna Heckman
- GCEP & GREF (Jeff, Milt, Mary)
- National Science Foundation
- U.S. EPA
- University of British Columbia



The Jaffe Research Group, from right:  
Arrie, Isaac, Julie, Dan, J.B., Peter, Anna, Heather,  
Phil

# What Now??

## PCC research with Dr. Lyatt Jaeglé

### Hydrogen and the GEOS-CHEM Model

H<sub>2</sub> is linked with greenhouse gas cycles:

CO, Methane, Formaldehyde (CH<sub>2</sub>O)

Possible future energy source as world moves away  
greenhouse gas emitting fossil fuels

Thus leading to a need to understand cycling of H<sub>2</sub>  
One way is to model H<sub>2</sub> and validate with  
measurements

# Questions for a hydrogen model

- What is the magnitude and seasonal variability of the microbial soil sink for  $\text{H}_2$ ?
- What are the relative contributions of biogenic and anthropogenic sources of  $\text{CH}_2\text{O}$ ?
- What is the global source of  $\text{CH}_2\text{O}$  in the troposphere?

Therefore I propose to add to GEOS-CHEM  
a  $\text{H}_2$  module that will simulate ---

emission, transport, chemistry, isotopic fractionation,  
and deposition of  $\text{H}_2$  and its deuterium isotope

# Hydrogen

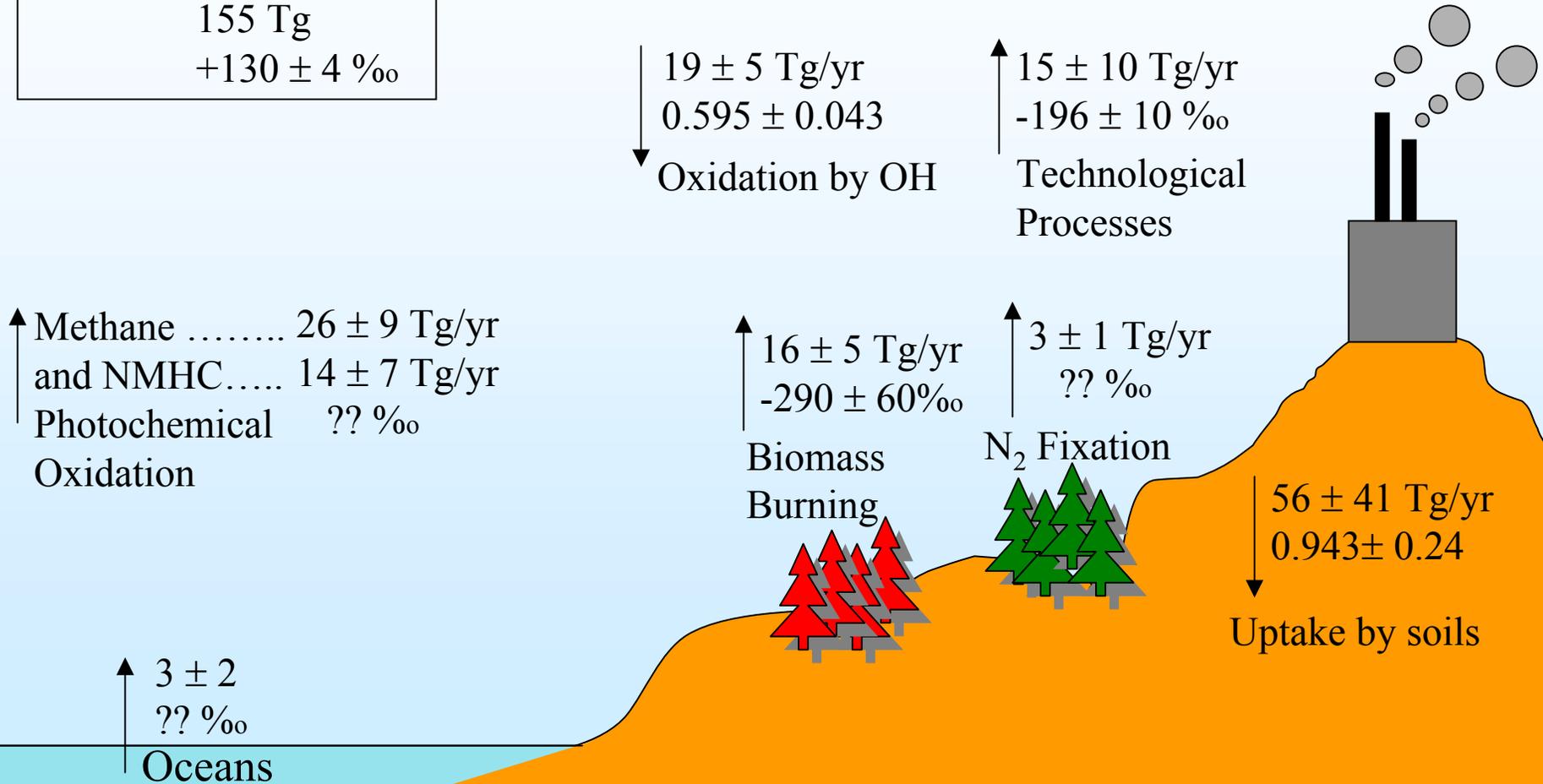
## H<sub>2</sub> in the troposphere:

Mixing ratio: ~530 ppb

S.H. abundance +3‰

155 Tg

+130 ± 4 ‰



Adapted from Gerst and Quay [2001, 2002] and Novelli et al. [1999]